COPROCESSING WITH PETROLEUM RESID AND MARTIN LAKE LIGNITE

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ABSTRACT

Petroleum resids have traditionally been overlooked as fuel sources despite their significant energy content. These products often contain iron, nickel, and vanadium in concentrations which rapidly deactivate or "poison" hydrogenation catalysts. Reacting petroleum resids with coal under liquefaction conditions or "coprocessing" has been proposed as an economic method for the removal of trace metals. Coprocessing involves the upgrading of a petroleum resid in a reaction with coal. While the resid acts as the liquefaction solvent some of the coal is converted to products, and the unconverted coal acts as a sink for metals. This paper will describe the results of tests to determine the increase in liquid product yields, and the reduction in the concentrations of trace metals achieved by coprocessing Arabian resid with Martin Lake lignite. Four batch-autoclave tests were made using various catalysts and conditions. Distillable products comprising 45-60 wt% of the individual product slurries were found to contain 2-8 ppm nickel and vanadium, and 9-41 ppm iron.

INTRODUCTION

Many petroleum resids contain iron, nickel, and vanadium. These contaminants are found in some resids in concentrations of several hundred parts per million (ppm), and can greatly reduce the value of a resid as a fuel source (1,2). Trace metals in general and vanadium in particular are known to deactivate or "poison" metal-based catalysts used in hydrogenation reactions to upgrade resids (3,4). As a catalyst becomes coated with metals its exposed, active surface area is gradually reduced, resulting in a decrease in catalytic activity (3,5). In order to hydrogenate resids and improve their potential as significant energy sources, trace metals concentrations must be economically reduced to tolerable levels. Several methods for accomplishing this have been studied including "coprocessing" (3,6-14). Coprocessing approaches the upgrading of petroleum resids as a concurrent process with the liquefaction of coal (15-23). While the resid acts as the liquefaction solvent some of the coal is converted to products, and the unconverted coal acts as a sink for metals.

In assessing the feasibility of coprocessing it may be necessary to consider a combination of three parameters rather than one. An ideal coprocessing reaction system would provide a product with minimal trace metals concentrations along with maximum amounts of converted coal and upgraded resid.

REACTION CONDITIONS

Data for this paper were obtained from the analysis of product slurries from four, two-stage batch autoclave tests with Martin Lake lignite and Lummus Arabian resid. Except for varying catalysts, reaction conditions for all four tests were essentially identical and are listed in Table 1.

TABLE 1

COPROCESSING REACTION CONDITIONS

	Test 1	Test 2	Test 3	Test 4
Stage 1				
Residence Time (min)	40	40	40	40
Temp (°C)	368	371	367	372
Pressure (psia)	4100	3875	4400	4370
Pressurizing Gas	CO	CO	CO	CO
Stage 2				
Residence Time (min)	10	10	10	10
Temp (°C)	425	423	433	425
Pressure (psia)	2225	2325	2950	2970
Pressurizing Gas	H_2	H_2	H_2	H_2
Catalyst (both stages)	none	H_2S	Ammonium Molybdate	none

It should be noted that the autoclave tests described in Table 1 were designated as runs N377, N379, N382, and N383 according to documentation procedures established at UNDEMRC. For the purpose of simplifying discussion, throughout this paper the tests will be referred to as Tests 1, 2, 3, and 4, respectively.

Table 2 provides data relating reactants charged and moisture- and ash-free (MAF) coal conversions achieved for each batch autoclave test. The data indicate that coal reactivity was increased by the presence of the catalysts, especially ammonium molybdate. Tests 1 and 4 were performed under nearly identical conditions to provide data on test-reproducibility, but gave substantially different conversions. There is speculation that the higher conversion achieved by Test 4 was influenced by the presence in the autoclave of residual ammonium molybdate from Test 3. A more complete discussion of the test results in reference to product mix, reaction conditions, and catalyst effects can be found in Rindt, et. al. (24).

ANALYSIS OF PRODUCT SLURRIES BASED ON PENTANE-SOLUBILITY

To determine trace metals concentrations in coprocessing products as a function of pentane-solubility, samples of the product slurries from Tests 2, 3, and 4 were separated into pentane-soluble and insoluble fractions. Both fractions, and the raw product slurries from each test were analyzed for iron, nickel, and vanadium using an acid digestion technique. The pentane-soluble fraction of Arabian resid, the raw resid, and raw

Martin Lake lignite were also analyzed according to the same procedure.

TABLE 2

COMPOSITIONS AND RESULTS OF BATCH AUTOCLAVE TESTS

	Test 1	Test 2	Test 3	Test 4
wt as-received coal (g)	134.5	139.6	141.7	142.8
wt MAF coal (g)	93.8	97.8	99.6	100.0
wt solvent (g)	350.5	365.5	372.2	373.7
wt water added (g)	16.7	17.0	18.0	17.4
wt FS* (g)	501.7	522.1	531.9	533.9
% FS that is MAF coal	18.7	18.7	18.7	18.7
wt PS** (g)	472.8	473.9	487.4	464.9
% THFI*** (PS)	11.5	9.7	7.2	11.0
% ash (PS)	4.5	4.4	4.5	4.7
% MAF coal unconverted	35.4	25.3	13.2	29.2
% MAF coal converted	64.6	74.7	86.8	70.8
catalyst	none	H_2S	ammonium molybdate	none

* Feed slurry
** Product slurry
*** Tetrahydrofuran insolubles

Sample sizes ranged from approximately 200 mg for the pentane insolubles, to 600 mg for the pentane solubles, to 1000 mg for the raw product slurries and the resid. The coal sample size was 220 mg. Samples were weighed into 250 mL "Nalgene" plastic containers equipped with screw-on lids. Nitric and hydrofluoric acid were added in 20 and 2 mL amounts, respectively. Lids were placed lightly, as opposed to screwed on the containers, which were then heated in a microwave oven in groups of two, for five minutes on "medium" power. The microwave oven power output was calculated according to a method published by Kingston and Jassie (25), and found to be approximately 330 watts on the medium setting. After cooling, 1 gram of boric and 20 mL of methanesulfonic acid were added to each sample, and the resulting mixtures were heated for 90 minutes at 110°C in the oven of a gas chromatograph. Both heating steps were performed under a hood to safely remove any escaping vapors. The use of methanesulfonic acid is recommended as an effective means of removing metals from porphyrin complexes (26). After vacuum filtration the mixtures were diluted to 100 mL with deionized water and analyzed using inductively-coupled plasma spectroscopy (ICP). Results of the analyses are shown in Table 3.

TABLE 3

METALS CONTENT BASED ON PENTANE-SOLUBILITY

	Fe (ppm)	Ni (ppm)	V (ppm)
Test 2 product slurry	1700	45	91
pentane solubles	0	0	6
pentane insolubles	13000	190	370
Test 3 product slurry	1800	47	70
pentane solubles	17	4	6
pentane insolubles	16000	210	360
Test 4 product slurry	2400	57	100
pentane solubles	46	0	5
pentane insolubles	13000	180	380
Arabian resid raw	56	37	120
pentane solubles	0	8	28
Martin Lake coal	4300	0	24
NBS 8505 certified*	-	-	390
analyzed**	8	57	460
NBS 1634a certified*	31	29	56
analyzed**	27	31	61

* Values certified by National Bureau of Standards.
** Values obtained using described analysis.

The bottom two entries in Table 3 refer to Standard Research Materials provided by the National Bureau of Standards, and were included as a means of determining the accuracy of the analytical method. The standards, NBS 8505, vanadium in crude oil (no values for iron or nickel) and NBS 1634a, trace metals in fuel oil residual, were similar in consistency and color to the coprocessing product slurries. Comparison of NBS certified values with values obtained through analysis suggests that the analytical method may yield an error of up to 18%.

Table 4 compares analytically-obtained metals concentration values for the three product slurries with values obtained using a mass balance calculation. The calculations were done using pentane solubilities and the metals concentration values for the pentane-soluble and pentane-insoluble fractions found in Table 3. As an example, the Test 2 calculated value for vanadium was obtained with the following formula: 74.6%(6) + 25.4%(370) = 98. Comparison of values for iron suggests that something more than analytical error is contributing to the large difference between analyzed and calculated values. One possible explanation may derive from the digestion procedure since the same amount of acid was used to digest all the samples, regardless of weight or iron concentration. Digestion of the pentane-insolubles, which

contained high concentrations of iron, was done using a small sample (200 mg). While digestion of the pentane-solubles utilized a larger sample (600 mg), the iron in the samples was much less concentrated. In the case of the product slurry samples, the combination of large sample size (1000 mg) and moderately high iron concentration may have resulted in an incomplete digestion due to an overabundance of iron in comparison to acid.

TABLE 4

COMPARISON OF ANALYZED METALS CONTENT TO MASS BALANCE CALCULATED METALS CONTENT OF PRODUCT SLURRIES (PENTANE SOLUBILITY BASIS)

	Pentane Solubility (%)	Fe (ppm)	Ni (ppm)	V (ppm)
Test 2	74.6			
Analyzed value		1700	45	91
Calculated value		3300	48	98
Test 3	77.4			
Analyzed value		1800	47	70
Calculated value		3600	51	86
Test 4	72.7			
Analyzed value		2400	57	100
Calculated value		3600	49	107

DISTILLATION OF PRODUCT SLURRIES

The effect of coprocessing on trace metals concentrations was also examined as a function of percent product slurry distillable. Vacuum distillations were carried out using Pyrex glassware with T 14/20 joints. Slow flowing water was used as the first stage condenser cooling fluid. A distillation column approximately 20 cm long was used to reduce the chance of non-distilled sample carryover or "bumping". The apparatus was fitted with a fractionating device and operated under a vacuum of about 5 torr as measured with a mercury-filled McLeod Gauge. Product slurry samples of 10 - 25 g were placed into a 30 ml round bottom flask, heated with a mantle, and stirred with a Teflon-coated magnetic stir bar. As heating progressed the system pressure was slowly reduced. In order to minimize the threat of bumping, the sample was stirred vigorously and the distillation column was warmed to 85°C using glass fabric heating tape. Heating the column allowed low-boiling volatile components to remain in the vapor phase instead of condensing and dripping back into the distillation pot. As the system pressure was gradually reduced to 5 torr, the voltage to the heating mantle was gradually increased to 130 volts, a process that took about 30 - 40 minutes.

The first fraction was collected until the temperature in the distillation head reached 120°C, and is identified as the initial boiling point (IBP) to 120°C fraction. Following collection of

the first fraction the water flow to the condenser was shut off and the condenser was drained. The remainder of the distillation was carried out using air as the condenser cooling fluid. The second fraction was collected over a temperature range of 120-260°C, and the third fraction was collected over a temperature range of 260°C to the "end point". The end point is defined as the temperature at which one or more of the following conditions exist: 1) the temperature in the head piece remains constant, 2) the temperature in the head piece is consistently falling, or 3) decomposition of the sample is evident (the sample remaining in the pot starts smoking). Two other fractions collected were the cold trap fraction and the pot residue. The cold trap fraction refers to the material collected in the cold trap, which is located between the distillation pot and the condenser, and cooled by a slurry bath of dry ice and 2-propanol. This material is a solid while in the cold trap, but becomes a volatile liquid at room temperature. The pot residue refers to the material remaining in the distillation pot after the end point has been reached and the distillation is complete. This fraction contains a solid phase and a very viscous liquid phase.

ANALYSIS OF PRODUCT SLURRIES BASED ON DISTILLATION CUTS

The technique used for the digestion of the distillates and residues (developed by David J. Hassett at the University of North Dakota Energy and Minerals Research Center) required a sample size of about 1 g. Placement of the sample in a 100 mL Pyrex volumetric flask was followed by the addition of 10 mL Ultrex concentrated sulfuric acid. The flask was then placed on a hot plate and the mixture was heated. When dense white fumes of sulfur trioxide began to appear, a few drops of concentrated Ultrex nitric acid were added to the mixture. The application of heat continued and dense white fumes of sulfur trioxide again began to appear, at which time several more drops of nitric acid were added. This cycle was repeated until the mixture became clear, or no darker than a dilute straw color. A clear solution indicates that the major portion of the organic matter has been oxidized. After cooling, the solution was diluted to 100 mL with deionized water and analyzed by ICP. A sample of Arabian resid was also distilled, digested, and analyzed according to the same procedure, except that only three distillate fractions were collected. Martin Lake coal was prepared for ICP analysis by two separate methods. One sample was digested and the other was ashed. Table 5 displays the results of these analyses.

Comparison of analytically-obtained values with NBS-certified values for NBS 1634a, trace metals in fuel oil residual, helps demonstrate the reliability of the analytical method. As another check on the analysis, Table 6 compares analytically-obtained metals concentration values for the product slurries and resid with values obtained using a mass balance calculation. The mass balance calculation is similar to the calculation used in Table 4 except that distillate percentages rather than pentane solubilities are used to multiply the metals concentration values in Table 6.

TABLE 5

METALS CONCENTRATIONS BASED ON PERCENT PRODUCT SLURRY DISTILLABLE

wt% product slurry		Fe (ppm)	Ni (ppm)	V (ppm)
Test 1 Prod. Slurry		4200	34	78
Cold trap	9.6	Below	detection	limits
IBP - 120°C	10.3	Below	detection	limits
120 - 260°C	31.7	7	4	4
260 - 275°C	6.2	75	40	40
Residue	42.2	10200	79	150
Test 2 Prod. Slurry		4000	37	81
Cold trap	4.4	Below	detection	limits
IBP - 120°C	13.6	Below	detection	limits
120 - 260°C	27.8	55	4	4
260 - 285°C	13.8	15	6	6
Residue	40.6	10200	99	180
Test 3 Prod. Slurry		4100	39	75
Cold trap	2.2	Below	detection	limits
IBP - 120°C	9.4	Below	detection	limits
120 - 260°C	30.5	12	4	4
260 - 305°C	16.1	7	6	6
Residue	37.3	10800	94	170
Test 4 Prod. Slurry		2700	30	65
Cold trap	2.7	Below	detection	limits
IBP - 120°C	14.6	Below	detection	limits
120 - 260°C	31.8	74	5	5
260 - 285°C	14.1	9	5	5
Residue	36.8	10500	130	260
Resid		1	36	12
120 - 260°C	26.1	1	2	1
260 - 295°C	16.3	26	2	2
Residue	57.6	14	62	19
Coal digested		3900	6	21
Coal ashed		4000	31	22
NBS 1634a analyzed		32	29	58
NBS 1634a certified		31	29	56

Since analyzed and calculated values are in reasonable agreement for Tests 1 - 3 and the resid, the large differences between values for Test 4 are probably due to a measurement error. With the exception of Test 4 the analyzed and calculated values for iron are very close, unlike the values in Table 4.

TABLE 6

ANALYZED METALS CONTENT COMPARED TO MASS BALANCE CALCULATED METALS CONTENT FOR PRODUCT SLURRIES (PERCENT DISTILLABLE BASIS)

	Fe (ppm)	Ni (ppm)	V (ppm)
Test 1			
Analyzed value	4200	34	78
Calculated value	4300	37	67
Test 2			
Analyzed value	4000	37	81
Calculated value	4200	42	75
Test 3			
Analyzed value	4100	39	75
Calculated value	4000	37	66
Test 4			
Analyzed value	2700	30	65
Calculated value	3900	50	98
Resid			
Analyzed value	1	36	12
Calculated value	13	37	12

This may be due to the digestion technique. While the first technique utilized a standard amount of acid for all samples, the amount of acid used in the second technique was individually determined for each sample based on the amount of oxidizable material contained in the sample. Calculated and analyzed values for nickel and vanadium in the resid are much closer than similar values for the product slurries from Tests 1 - 3. This could be because their were fewer chances for analytical error in the resid analysis since only three distillate fractions were obtained, as opposed to five for the product slurries.

COMPARISON OF DIGESTION TECHNIQUES

Table 7 compares analyzed metals concentration values for the product slurries to values that were expected based on feed slurry composition data. All analytical data in Table 7 are the result of analyses using the methanesulfonic acid digestion technique. The metals contents of the coal and resid were used to calculate the total metals content in grams for each slurry charged in the autoclave. By assuming grams metal in feed slurry equals grams metal in product slurry for the three metals, ppm values were calculated based on the weight of total product slurry recovered. Also included in the table is the ratio of expected value to analyzed value for the three metals in each test.

TABLE 7

EXPECTED COMPARED TO ANALYZED METALS CONTENTS BASED ON METHANESULFONIC ACID DIGESTIONS

	Fe (ppm)	Ni (ppm)	V (ppm)
Test 2 expected	1300	29	93
Test 2 analyzed	1700	45	91
expected / analyzed	0.76	0.64	1.02
Test 3 expected	1300	28	99
Test 3 analyzed	1800	47	70
expected / analyzed	0.72	0.60	1.41
Test 4 expected	1400	30	104
Test 4 analyzed	2400	57	100
expected / analyzed	0.58	0.53	1.04

Table 8 also compares analyzed metals contents of the product slurries to expected metals contents based on feed slurry composition data. All analytical data in Table 8 are the result of analyses using the Ultrex acid digestion technique.

TABLE 8

EXPECTED COMPARED TO ANALYZED METALS CONTENTS BASED ON ULTREX ACID DIGESTIONS

	Fe (ppm)	Ni (ppm)	V (ppm)
Test 1 expected	1100	28	15
Test 1 analyzed	4200	34	78
expected / analyzed	0.26	0.82	0.19
Test 2 expected	1200	30	16
Test 2 analyzed	4000	37	81
expected / analyzed	0.30	0.81	0.20
Test 3 expected	1200	29	16
Test 3 analyzed	4100	39	75
expected / analyzed	0.29	0.74	0.21
Test 4 expected	1200	31	16
Test 4 analyzed	2700	30	65
expected / analyzed	0.44	1.03	0.24

The most consistent relationship between analyzed and expected values in either Table 7 or Table 8 is evident in the comparison

of ratios for Tests 1 - 3 in the Ultrex acid digestion matrix. Although the analyzed values do not match the expected values, they are reasonably precise and consistent in their variation from the expected values. (Data from Test 4 do not correlate well with data from Tests 1 - 3, but, as previously discussed, it appears likely an error was made, in either the processing or analysis of the Test 4 product slurry.) The ratios displayed in Table 8 indicate that a greater degree of analytical precision is achievable through the use of the Ultrex acid digestion. The consistent variation in analyzed values suggests that a consistently performed step in the reaction process is responsible for the inaccuracy of the analyzed values. The higher than expected analyzed values for iron may be a result of storing the product slurries in metal cans upon their removal from the autoclave.

COMPARISON OF PRODUCT RECOVERY METHODS

Pentane extraction and distillation were compared as methods of recovering the largest product yield with the lowest metals concentrations possible. Table 9 displays metals contents as a function of pentane solubility, along with coal conversions achieved for tests 2, 3, and 4. Pentane solubility and pentane-solubles metals contents are also included for the Arabian resid.

TABLE 9

METALS CONTENT AS A FUNCTION OF PENTANE-SOLUBILITY

	Pentane Solubility (%)	Fe (ppm)	Ni (ppm)	V (ppm)	% MAF coal converted
Test 2	74.6	0	0	6	74.7
Test 3	77.4	17	4	6	86.8
Test 4	72.7	46	0	5	70.8
Resid	80.3	0	8	28	

The data in Table 9 suggest that coprocessing may have potential as a means of reducing nickel and vanadium concentrations in the pentane-soluble fraction of Arabian resid. Since the feed slurries for the autoclave tests contained approximately 72% resid by weight, if no metals were removed during coprocessing, the pentane-soluble fraction of the product slurries should contain about 72% of 28 ppm, or 20 ppm vanadium. (Although this calculation is meaningful, it is not absolutely correct since it does not account for some gas production during the reaction and slight differences in pentane solubilities.)

Table 10 displays metals contents as a function of total product slurry distillable, along with coal conversions for the four tests. Similar data is included for the resid.

TABLE 10

METALS CONTENT AS A FUNCTION OF TOTAL DISTILLATE

	% Distillable	Fe (ppm)	Ni (ppm)	V (ppm)	% MAF coal Converted
Test 1	45	15	7.8	7.8	64.6
Test 2	54	32	3.5	3.5	74.7
Test 3	54	8.7	1.7	1.7	86.8
Test 4	60	41	3.8	3.8	70.8
Resid	42	11	2.0	1.4	

CONCLUSIONS

On the basis of this preliminary study, coprocessing appears to have merit as a means of reducing catalyst-poisoning metals concentrations in petroleum resids. However, in order to properly evaluate coprocessing, coal conversion and extent of resid-upgrading need to be assessed in terms of reaction cost and product value. Also, a larger, more accurate analytical data base is required to validate the metals concentration values.

According to this study, pentane extraction of the product slurry provides a greater usable product yield than distillation, and the pentane-soluble product contains iron, nickel, and vanadium in concentrations comparable to those of the distillate product. However, because of more and greater inconsistencies in data acquired using the methanesulfonic acid digestion, in order to properly compare product recovery methods it would be necessary to analyze a sample matrix based on pentane-solubility using the Ultrex acid digestion.

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